replanding

Claims:

1. Use of compounds of formula (I):

$$(R^{1})_{n} \xrightarrow{X} (R^{2})_{m}$$

$$N = N - R^{3}$$

$$(I)$$

5 wherein

- X is sulfur, oxygen, sulfinyl (S=O), sulfonyl (SO<sub>2</sub>), NR<sup>a</sup>, or CR<sup>b</sup>R<sup>c</sup>;
  - R<sup>a</sup> hydrogen, C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>2</sub>-C<sub>6</sub>-alkenyl, or C<sub>2</sub>-C<sub>6</sub>-alkynyl, wherein the carbon atoms in these groups may be substituted by 1 to 3 groups R<sup>#</sup>
    - R\* halogen, cyano, nitro, hydroxy, mercapto, amino, C<sub>1</sub>-C<sub>6</sub>-alkylcarbonylamino, carboxyl, C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkoxy, C<sub>2</sub>-C<sub>6</sub>-alkenyloxy, C<sub>2</sub>-C<sub>6</sub>-alkynyloxy, C<sub>1</sub>-C<sub>6</sub>-haloalkoxy, or C<sub>1</sub>-C<sub>6</sub>-alkylthio;

phenyl or benzyl, each unsubstituted or substituted with any combination of 1 to 5 halogen, 1 to 3  $C_1$ - $C_6$ -alkyl,  $C_1$ - $C_6$ -haloalkylthio,  $C_1$ - $C_6$ -haloalkylthio,  $C_1$ - $C_6$ -haloalkylthio,  $C_1$ - $C_6$ -haloalkoxy groups;

 $R^b$ ,  $R^c$  are each independently hydrogen,  $C_1$ - $C_6$ -alkyl,  $C_2$ - $C_6$ -alkenyl,  $C_2$ - $C_6$ -alkinyl,  $C_1$ - $C_6$ -hydroxyalkyl, wherein the carbon atoms in these groups may be substituted by 1 to 3 groups  $R^\#$ , or

phenyl, unsubstituted or substituted with any combination of 1 to 5 halogen, 1 to 3  $C_1$ - $C_6$ -alkyl,  $C_1$ - $C_6$ -haloalkyl,  $C_1$ - $C_6$ -alkoxy or  $C_1$ - $C_6$ -haloalkoxy groups, or

 $CR^bR^c$  represents C=O or C= $CR^jR^k$ , wherein  $R^j$  and  $R^k$  each independently are hydrogen, halogen,  $C_1$ - $C_6$ -alkyl,  $C_1$ - $C_6$ -haloalkyl, or  $C_3$ - $C_6$ -cycloalkyl;

 $R^1$ ,  $R^2$  are each independently halogen, hydroxy, mercapto, amino, cyano, nitro,  $C_1$ - $C_6$ -alkyl,  $C_1$ - $C_6$ -alkoxy,  $C_1$ - $C_6$ -alkylamino, di( $C_1$ - $C_6$ -alkyl)amino,  $C_1$ - $C_8$ -alkylthio,  $C_2$ - $C_6$ -alkenyl,  $C_2$ - $C_6$ -alkenyloxy,  $C_2$ - $C_6$ -alkynylamino,  $C_2$ - $C_6$ -alkynyl,  $C_2$ - $C_6$ -alkynyloxy,  $C_2$ - $C_6$ -alkynylamino,  $C_2$ - $C_6$ -alkynyloxy,  $C_2$ - $C_6$ -

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alkynylthio, C<sub>1</sub>-C<sub>6</sub>-alkylsulfonyl, C<sub>1</sub>-C<sub>6</sub>-alkylsulfoxyl, C<sub>2</sub>-C<sub>6</sub>-alkenylsulfonyl, C<sub>2</sub>-C<sub>6</sub>-alkynylsulfoxyl, formyl, C<sub>1</sub>-C<sub>6</sub>-alkylcarbonyl, hydroxycarbonyl, C<sub>1</sub>-C<sub>6</sub>alkoxycarbonyl, carbonyloxy, C<sub>1</sub>-C<sub>6</sub>-alkylcarbonyloxy, phenyloxy, C<sub>1</sub>-C<sub>6</sub>alkylcarbonylamino, C(O)NR<sup>d</sup>R<sup>e</sup>, or (SO<sub>2</sub>)NR<sup>d</sup>R<sup>e</sup>, wherein the carbon atoms 5 in the aliphatic and aromatic groups may be substituted by 1 to 3 groups R# and wherein R<sup>d</sup> and R<sup>e</sup> are each independently groups as listed for R<sup>a</sup>; or C(=NORf)-G<sub>p</sub>-Rf, wherein Rf and Rf are each independently hydrogen or C<sub>1</sub>-C<sub>6</sub>-alkyl, G is oxygen, sulfur or NR<sup>f</sup> and p is 0 or 1; or 10 a mono- or bicyclic 5- to 10-membered aromatic ring system which may contain 1 to 4 heteroatoms selected from oxygen, sulfur and nitrogen and which is unfused or fused to the aromatic group to which it is bonded and which, when unfused, is bonded directly or through an oxygen, sulfur, C<sub>1</sub>-15 C<sub>6</sub>-alkyl, or C<sub>1</sub>-C<sub>6</sub>-alkoxy linkage, and which is unsubstituted or substituted with any combination of 1 to 5 groups R#; or C<sub>3</sub>-C<sub>12</sub>-cycloalkyl, which is bonded directly or through an oxygen, sulfur or C<sub>1</sub>-C<sub>6</sub>-alkyl linkage, and which is unsubstituted or substituted with any com-20 bination of 1 to 5 groups R#; R<sup>3</sup>,R<sup>4</sup> are each independently hydrogen, C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-haloalkyl, C<sub>1</sub>-C<sub>6</sub>alkylamino, C<sub>1</sub>-C<sub>6</sub>-alkoxy, C<sub>3</sub>-C<sub>6</sub>-cycloalkyl, wherein the carbon atoms in these groups may be substituted with any combination of 1 to 3 groups R#, or C(O)R<sup>9</sup>, C(O)NR<sup>h</sup>R<sup>i</sup>, or C(S)NR<sup>h</sup>R<sup>i</sup>, 25  $R^g$ hydrogen, C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkoxy, or phenyl or benzyl, each unsubstituted or substituted with any combina-30 tion of 1 to 5 halogen, 1 to 3 C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-haloalkyl, C<sub>1</sub>-C<sub>6</sub>alkylthio, C<sub>1</sub>-C<sub>6</sub>-haloalkylthio, C<sub>1</sub>-C<sub>6</sub>-alkoxy or C<sub>1</sub>-C<sub>6</sub>-haloalkoxy groups; R<sup>h</sup>,R<sup>i</sup> are each independently groups as listed for R<sup>a</sup>;

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or R³ and R⁴ together with the nitrogen atom to which they are attached form a saturated or partially saturated mono- or bicyclic 5- to 10-membered ringsystem containing 1 to 3 heteroatoms selected from nitrogen and oxygen or 5-membered hetaryl containing 1 to 4 nitrogen atoms, wherein the carbon and/or nitrogen atoms in the satu-

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rated, partially saturated or aromatic rings are unsubstituted or substituted with any combination of 1 to 4 groups selected from amino, C<sub>1</sub>- $C_6$ -alkyl,  $C_2$ - $C_6$ -alkenyl,  $C_2$ - $C_6$ -alkynyl,  $C_1$ - $C_6$ -alkoxy,  $C_2$ - $C_6$ -alkenyloxy,  $C_2$ - $C_6$ -alkynyloxy,  $C_1$ - $C_6$ -alkylthio,  $C_2$ - $C_6$ -alkenylthio,  $C_2$ - $C_6$ -alkynylthio, C<sub>1</sub>-C<sub>6</sub>-alkylamino, di(C<sub>1</sub>-C<sub>6</sub>-alkyl)amino, C<sub>2</sub>-C<sub>6</sub>-alkenylamino, C<sub>2</sub>-C<sub>6</sub>alkynylamino, C<sub>1</sub>-C<sub>6</sub>-hydroxyalkyl, hydroxycarbonyl-C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkoxycarbonyl-C<sub>1</sub>-C<sub>4</sub>-alkyl, formyl-C<sub>1</sub>-C<sub>4</sub>-alkyl, formyl-C<sub>1</sub>-C<sub>4</sub>alkoxy, C<sub>1</sub>-C<sub>6</sub>-alkylcarbonyl-C<sub>1</sub>-C<sub>4</sub>-alkoxy, C<sub>3</sub>-C<sub>6</sub>-cycloalkyl, which is bonded directly or via an oxygen, sulfur or C<sub>1</sub>-C<sub>6</sub>-alkyl linkage, and C<sub>5</sub>-C<sub>8</sub>-cycloalkenyl, wherein the carbon atoms in these aliphatic groups can be substituted by 1 to 4 groups selected from halogen, cyano, hydroxy and nitro; or phenyl or benzyl which may be substituted by halogen, C<sub>1</sub>-C<sub>4</sub>-alkyl or C<sub>1</sub>-C<sub>4</sub>-haloalkyl; or  $R^3$  and  $R^4$  together form the chains  $-(CH_2)_2N^+(O^-)(CH_2)_2$  or -

 $(CH_2)_3N^+(O^-)(CH_2)_2-;$ 

is 0, 1, 2, 3 or 4; m

is 0, 1, 2, 3 or 4; 20 n

> or the enantiomers or diastereomers, salts or esters thereof for combatting insects, arachnids, or nematodes.

- A method for controlling insects, arachnids or nematodes comprising contacting 25 2. an insect, arachnid or nematode or their food supply, habitat or breeding grounds with a pesticidally effective amount of compounds of formula I as defined in claim 1 or compositions comprising them.
- A method for protecting growing plants from attack or infestation by insects, a-30 . 3. rachnids or nematodes comprising contacting a plant, or soil or water in which the plant is growing, with a pesticidally effective amount of compounds of formula I as defined in claim 1 or compositions comprising them.
- 35 A process for the preparation of compounds of formula I-A 4.

$$(R^{1})_{n} \xrightarrow{S} (R^{2})_{m}$$

$$N = (I-A)$$

$$N = (I-A)$$

$$R^{z}$$

wherein  $R^z$  is hydrogen, amino,  $C_1$ - $C_6$ -alkyl,  $C_2$ - $C_6$ -alkenyl,  $C_2$ - $C_6$ -alkynyl,  $C_1$ - $C_6$ -alkoxy,  $C_2$ - $C_6$ -alkenyloxy,  $C_2$ - $C_6$ -alkynyloxy,  $C_1$ - $C_6$ -hydroxyalkyl, hydroxycarbonyl- $C_1$ - $C_4$ -alkyl,  $C_1$ - $C_6$ -alkoxycarbonyl- $C_1$ - $C_4$ -alkyl, formyl- $C_1$ - $C_4$ -alkyl, formyl- $C_1$ - $C_4$ -alkoxy,  $C_1$ - $C_6$ -alkylcarbonyl- $C_1$ - $C_4$ -alkoxy,  $C_3$ - $C_6$ -cycloalkyl, which is bonded directly or through an oxygen, sulfur or  $C_1$ - $C_6$ -alkyl linkage, or  $C_5$ - $C_8$ -cycloalkenyl, wherein the carbon atoms in these aliphatic groups can be substituted by 1 to 4 groups selected from halogen, cyano, hydroxy and nitro; or phenyl or benzyl which may be substituted by halogen,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -haloalkyl; and wherein the group [N-R²] may be present as amine oxide [N¹(O¹)-R²]; o is 1 or 2, and the further variables and the indices are as defined for formula I in claim 1, wherein in a first step o-amino-thiophenol derivatives of formula II

$$(R^1)_n$$
  $NH_2$  (II)

wherein R<sup>1</sup> and n are as defined for formula I in claim 1 are reacted with benzoic acid derivates III

Hal
$$(R^2)_m$$
 (III)

wherein Hal is halogen and R<sup>2</sup> and m are as defined for formula I in claim 1 in the presence of a base and a transition metal (I) oxide or - halogenid as catalyst to give compounds IV,

$$(R^1)_n$$
 $(R^2)_m$ 
 $(IV)$ 

which compounds are further reacted with a halogenating agent to yield compounds of formula V

$$(R^1)_n$$
  $(V)$ 

wherein Hal\* is halogen which after reaction with piperazine derivates VI

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wherein o and Rz are as defined for formula I-A give compounds I-A.

5. A process for the preparation of compounds of formula I-B

$$(R^1)_n$$
 $O$ 
 $(R^2)_m$ 
 $N = (I-B)$ 
 $N = (I-B)$ 
 $R^2$ 

wherein the variables and the indices are as defined for formula I-A in claim 5 wherein in a first step o-amino-phenol derivatives of formula VII

$$(R^1)_n$$
  $OH$   $NH_2$  (VII)

wherein R<sup>1</sup> and n are as defined for formula I in claim 1 are reacted with benzoic acid derivates III\*

$$\begin{array}{ccc}
\text{Hal} \\
\text{Y} & & \\
\text{O}
\end{array}$$

$$(III*)_{m} & (III*)_{m}$$

wherein Hal is halogen, Y is hydroxy, halogen or  $C_1$ - $C_6$ -alkoxy and  $R^2$  and m are as defined for formula I in claim 1 to give compounds VIII,

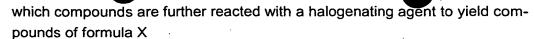
$$(R^{1})_{n} \xrightarrow{\text{OH}} (R^{2})_{m} \qquad (VIII)$$

which in a second step are cyclizized in the presence of a base to give compounds IX

$$(R^1)_n$$
  $(R^2)_m$   $(IX)$ 

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$$(R^1)_n$$
 $(R^2)_m$ 
 $(X)$ 

wherein the variables and the indices have the meanings as defined for formula I and Hal\* is halogen which after reaction with piperazine derivates VI as defined in claim 5 give compounds I-B.

## 6. Compounds of formula I-A

$$(R^{1})_{n}$$

$$N = (I-A)$$

$$N = (I-A)$$

$$R^{z}$$

10 wherein

R<sup>1</sup>,R<sup>2</sup> are each independently halogen, hydroxy, mercapto, amino, cyano, nitro, C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkoxy, C<sub>1</sub>-C<sub>6</sub>-alkylamino, di(C<sub>1</sub>-C<sub>6</sub>-alkyl)amino, C<sub>1</sub>-C<sub>8</sub>-alkylthio, C<sub>2</sub>-C<sub>6</sub>-alkenyl, C<sub>2</sub>-C<sub>6</sub>-alkenyloxy, C<sub>2</sub>-C<sub>6</sub>-alkenylamino, C<sub>2</sub>-C<sub>6</sub>-alkenylthio, C<sub>2</sub>-C<sub>6</sub>-alkynyl, C<sub>2</sub>-C<sub>6</sub>-alkynyloxy, C<sub>2</sub>-C<sub>6</sub>-alkynylamino, C<sub>2</sub>-C<sub>6</sub>-alkynylthio, C<sub>1</sub>-C<sub>6</sub>-alkylsulfonyl, C<sub>2</sub>-C<sub>6</sub>-alkenylsulfonyl, formyl, or C<sub>1</sub>-C<sub>6</sub>-alkylcarbonyl, wherein the carbon atoms in the aliphatic and aromatic groups may be substituted by 1 to 3 groups selected from halogen, cyano, nitro, hydroxy, mercapto, amino, C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkoxy, C<sub>2</sub>-C<sub>6</sub>-alkynyloxy, C<sub>1</sub>-C<sub>6</sub>-haloalkoxy, or C<sub>1</sub>-C<sub>6</sub>-alkylthio;

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R<sup>z</sup> is hydrogen,  $C_1$ - $C_6$ -alkyl,  $C_2$ - $C_6$ -alkenyl,  $C_2$ - $C_6$ -alkynyl,  $C_1$ - $C_6$ -hydroxyalkyl,  $C_3$ - $C_6$ -cycloalkyl,  $C_3$ - $C_6$ -cycloalkyl- $C_1$ - $C_6$ -alkyl, or  $C_5$ - $C_8$ -cycloalkenyl, wherein the carbon atoms in these aliphatic groups can be substituted by 1 to 4 groups selected from halogen, cyano, hydroxy and nitro; and wherein the group [N-R<sup>z</sup>] may be present as amine oxide [N<sup>+</sup>(O)-R<sup>z</sup>];

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m is 1, 2, 3, or 4;

n is 1, 2, 3, or 4; and

o is 1 or 2.

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- 7. Compounds of formula I-A according to claim 6 wherein R<sup>1</sup> and R<sup>2</sup> each independently are halogen, C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-haloalkyl, methoxy, C<sub>1</sub>-C<sub>6</sub>-haloalkoxy, C<sub>1</sub>-C<sub>8</sub>-alkylthio, C<sub>1</sub>-C<sub>6</sub>-haloalkylthio, C<sub>2</sub>-C<sub>6</sub>-alkenylthio, or C<sub>2</sub>-C<sub>6</sub>-alkynylthio.
- 5 8. Compounds of formula I-B

$$(R^1)_n^{7}$$
 $(R^2)_m$ 
 $(I-B)$ 
 $(I-B)$ 

wherein R<sup>z</sup> and the indices n, m, and o are as defined for formula I-A in claim 6 and R<sup>1</sup> and R<sup>2</sup> each independently are halogen, C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-haloalkyl, methoxy, C<sub>1</sub>-C<sub>6</sub>-haloalkoxy, C<sub>1</sub>-C<sub>8</sub>-alkylthio, C<sub>1</sub>-C<sub>6</sub>-haloalkylthio, C<sub>2</sub>-C<sub>6</sub>-alkenylthio, or C<sub>2</sub>-C<sub>6</sub>-alkynylthio, with the proviso that when R<sup>1</sup> is 2-chloro then R<sup>2</sup> is not 8-chloro or 8-methoxy; and when R<sup>1</sup> is 4-chloro then R<sup>2</sup> is not 8-chloro; and when R<sup>1</sup> is 4-methyl then R<sup>2</sup> is not 7-, 8-, or 9-chloro.

## 15 9. Compounds of formula I-C

wherein  $R^a$  is hydrogen or  $C_1$ - $C_6$ -alkyl and the further variables and indices are as defined for formula I-B in claim 8, with the proviso that not both of  $R^1$  or  $R^2$  are halogen and when  $R^1$  is 2-chloro then  $R^2$  is not 8-methyl, 8-methylthio, or 8-methoxy; and

when R<sup>1</sup> is 2-chloro then R<sup>2</sup> is not 8-methyl, 8-methylthio, or 8-methoxy; and when R<sup>1</sup> is 2-methoxy, then R<sup>2</sup> is not 8-chloro; and when R<sup>1</sup> is 2-methyl then R<sup>2</sup> is not 8-chloro.

## 10. Compounds of formula I-D

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wherein R<sup>b</sup> and R<sup>c</sup> are each independently hydrogen, methyl or CR<sup>b</sup>R<sup>c</sup> represents C=CH<sub>2</sub>, and the further variables and the indices are as defined for formula I-B in claim 8.

11. Compositions comprising compounds of formula I-A, I-B, I-C, and/or I-D as defined in claims 6 to 10 or the enantiomers or diastereomers, salts or esters thereof and an agronomically acceptable carrier.